METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY-- DETERMINATION OF ORGANONITROGEN HERBICIDES IN WATER BY SOLID-PHASE EXTRACTION AND CAPILLARY-COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY WITH SELECTED-ION MONITORING

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Open-File Report 91-519

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	3.94×10^{-1}	inch
inch (in.)	25.4	millimeter
gram (g)	3.53×10^{-2}	ounce
kilopascal (kPa)	0.296	inch of mercury (Hg)
liter (L)	0.265	gallon
meter (m)	3.28	foot
microgram (µg)	3.53×10^{-8}	ounce
microliter (µL)	2.64×10^{-7}	gallon
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce
milliliter (mL)	2.64×10^{-4}	gallon
milliliter per minute (mL/min)	3.38×10^{-2}	ounce per minute
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

The following terms and abbreviations also are used in this report:

°C/min	degrees Celsius per minute
GC/MS	gas chromatograph/mass spectrometer
ID	inside diameter
MDL	method detection limit
µg/L	microgram per liter
ng/µL	nanogram per microliter
OD	outside diameter
PAH	polyaromatic hydrocarbon
PFTBA	perfluorotributylamine
RT	retention time
SIM	selected-ion monitoring
SPE	solid-phase extraction
Teflon-PFA	Teflon-perfluoroalkoxy
Tefzel-ETFE	Tefzel-ethylenetetrafluoroethylene

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ABSTRACT

A method for the isolation of organonitrogen herbicides from natural water samples using solid-phase extraction and analysis by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring is described. Water samples are filtered to remove suspended particulate matter and then are pumped through disposable solid-phase extraction cartridges containing octadecyl-bonded porous silica to remove the herbicides. The cartridges are dried using carbon dioxide, and adsorbed herbicides are removed from the cartridges by elution with 1.8 milliliters of hexane-isopropanol (3:1). Extracts of the eluants are analyzed by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring of at least three characteristic ions. The method detection limits are dependent on sample matrix and each particular herbicide. The method detection limits, based on a 100-milliliter sample size, range from 0.02 to 0.25 microgram per liter. Recoveries averaged 80 to 115 percent for the 23 herbicides and 2 metabolites in 1 reagent-water and 2 natural-water samples fortified at levels of 0.2 and 2.0 micrograms per liter.

INTRODUCTION

Organonitrogen herbicides include some of the most widely used agricultural pesticides (Gianessi and others, 1986). They also are the most frequently detected pesticides in ground water in the United States (Hallberg, 1989) and Europe (Leistra and Boesten, 1989). The traditional method for determining residues of these herbicides in natural-water samples involves

liquid-liquid extraction with an organic solvent followed by analysis by gas chromatography with nitrogen-phosphorus detection, using two columns for confirmation of herbicide identity.

Recently, methods for herbicide analysis using solid-phase extraction (SPE) as an alternative to liquid-liquid extraction have been described (Bagnati and others, 1988; Bellar and Budde, 1988; Eichelberger and others, 1988; Junk and Richard, 1988; Battista and others, 1989; Brooks and others, 1989; DiCorcia and others, 1989; Sandstrom, 1989; Thurman and others, 1990). These SPE methods are attractive because they are rapid, efficient, use less solvents than liquid-liquid extraction, and consequently have lesser laboratory expenses. The SPE methods can be conducted at the field site, which enables processing of samples with labile analytes or processing samples at remote sites. In addition, the SPE methods can be automated by using laboratory robotic systems that do all or part of the sample-preparation steps. Some of these SPE methods also incorporate the use of a gas chromatograph/mass spectrometer (GC/MS) operated under full scan and in a selected-ion monitoring (SIM) mode for confirmation and quantitation of herbicides. The GC/MS is a more sensitive and more specific detector than is the nitrogen-phosphorus detector.

This report describes a method for determining organonitrogen herbicides developed by the U.S. Geological Survey for use in the Survey's National Water Quality Laboratory. The method incorporates SPE for removal of the herbicides from water samples and a GC/MS operated in the SIM mode for selective confirmation and quantitation of the herbicides. The method supplements other methods of the U.S. Geological Survey for determination of organic substances in water that are described by Wershaw and others (1987). The method was implemented in the National Water Quality Laboratory in March 1991.

This report provides a detailed description of all aspects of the method from sampling protocol through calculation and reporting of results. Precision and accuracy data, and method detection limits for 23 organo-nitrogen herbicides and 2 metabolites of atrazine--desethylatrazine and desisopropylatrazine--are presented.

ANALYTICAL METHOD

Parameters: Organonitrogen herbicides, dissolved, O-1121-91 (See table 1 for codes.)

1. Scope and application

This method is suitable for the determination of selected organonitrogen herbicides and metabolites in natural-water samples containing at least 0.05 µg/L of each herbicide or metabolite. The method is applicable to herbicides and metabolites that are: (1) Efficiently partitioned from the water

phase onto an octadecyl (C-18) organic phase that is chemically bonded to a solid inorganic matrix; and (2) sufficiently volatile and thermally stable for gas chromatography. Suspended particulate matter is removed from the samples by filtration, so this method is suitable only for dissolved-phase herbicides and metabolites. The method was used to determine the concentrations of the 23 herbicides and the 2 metabolites of atrazine--desethylatrazine and desisopropylatrazine--listed in table 1. The 23 herbicides are those in the current (1991) National Water Quality Laboratory schedule 1389, which includes herbicides added to the schedule as part of the U.S. Geological Survey's National Water Quality Assessment Program.

Previously completed development of the method (Sandstrom, 1989), as well as other comparable methods (Thurman and others, 1990) served as background for this report. Testing of the method included adjustment of sample volume and final extract volume to optimize recovery of the herbicides, especially the metabolites of atrazine--desethylatrazine and desisopropylatrazine.

2. Summary of method

2.1 Water samples (100 mL) are filtered to remove suspended particulate matter. Glass-fiber filters with a nominal 0.7-µm pore diameter or disposable, in-line filter units, containing a nylon membrane with a nominal 0.45-µm pore diameter depending on the concentration of the suspended particulate matter in the water samples, are used.

2.2 Filtered water samples are pumped through disposable, polypropylene SPE cartridges containing 0.5 g of porous silica coated with a C-18 organic phase that is chemically bonded to the surface of the silica.

2.3 The SPE cartridges are dried using a gentle stream of carbon dioxide to remove interstitial water.

2.4 The adsorbed herbicides and metabolites are removed from the SPE cartridges by elution with 1.8 mL of hexane-isopropanol (3:1).

2.5 The eluant is further evaporated using a gentle stream of nitrogen to a final volume of 100 µL.

2.6 Extracts of the eluant are analyzed by a capillary-column GC/MS operated in the SIM mode.

3. Interferences

Organic compounds having gas-chromatographic retention times and characteristic ions with a mass identical to those of the herbicides and metabolites of interest may interfere.

Table 1.--*Constituent codes, laboratory codes, and Chemical Abstracts Service registry numbers for method analytes*

[CAS, Chemical Abstracts Service; --, no code assigned]

Herbicide or metabolite	Constituent code	Laboratory code	CAS number
Alachlor	46342	1587	15972-60-8
Ametryn	38401	1588	834-12-8
Atrazine	39632	1589	1912-24-9
Bromacil	--	--	314-40-9
Butachlor	--	--	23184-66-9
Butylate	--	--	2008-41-5
Carboxin	--	--	5234-68-4
Cyanazine	--	1590	21725-46-2
Cycloate	--	--	1134-23-2
Desethylatrazine	--	1591	6190-65-4
Desisopropylatrazine	--	1592	1007-28-9
Diphenamid	--	--	957-51-7
Hexazinone	--	--	51235-04-2
Metolachlor	39415	1593	51218-45-2
Metribuzin	82360	1594	21087-64-9
Prometon	--	1597	1610-18-0
Prometryn	--	1598	7287-19-6
Propachlor	--	--	1918-16-7
Propazine	38535	1595	139-40-2
Simazine	--	1596	122-34-9
Simetryn	--	--	1014-70-6
Terbacil	--	--	5902-51-2
Terbuthylazine	--	--	5915-41-3
Trifluralin	--	--	1582-09-8
Vernolate	--	--	1929-77-7

4. Apparatus and equipment

4.1 The apparatus and equipment required for this method are listed as follows; specific sources and models used during the development of this method also are listed, where applicable:

4.1.1 Sample containers--125-mL, amber glass bottles fitted with Teflon-lined[1] screw caps.

[1] The use of trade and brand names in this report is for identification purposes only, and does not constitute endorsement by the U.S. Geological

4.1.2 Pipetting needles--Stainless steel, 16 gage [1.65 mm outside diameter (OD)], blunt tip with Luer-Lok fitting, 2.54-cm long; Popper and Sons, Inc.

4.1.3 Cleaning/elution module for SPE cartridges; Supelco, Inc., Visiprep Solid Phase Extraction Vacuum Manifold and Visidry Drying Attachment or equivalent.

4.1.4 Ceramic-piston, valveless metering pump with fittings for 1/8-in. OD tubing; Fluid Metering Inc., Model QSY-2 CKC or equivalent.

4.1.5 Teflon-perfluoroalkoxy (Teflon-PFA) tubing, 1/8-in OD; Cole-Parmer Instrument Co., CL-06375-01 or equivalent.

4.1.6 Tefzel-ethylenetetrafluoroethylene (Tefzel-ETFE) female Luer connector with 1/4-28 thread, Tefzel-ETFE union with 1/4-28 thread, and Tefzel-ETFE nut with 1/4-28 thread and 1/8-in. OD tubing connector; Upchurch Scientific.

4.1.7 Bottle-top solvent dispenser, 1 to 5 mL; Brinkmann Dispensette.

4.1.8 Vacuum pump--Any vacuum pump with sufficient capacity to maintain a slight vacuum of 1.5 to 3 kPa in the cleaning/elution module.

4.1.9 Micropipettes--50- and 100-µL, fixed- and variable-volume micropipettes with disposable glass capillaries; VWR Scientific.

4.1.10 Analytical balance--Any analytical balance capable of accurately weighing 150 g ± 0.1 g.

4.1.11 Fused-silica capillary column--Any fused-silica capillary column that provides adequate resolution, capacity, accuracy, and precision. A 25-m x 0.25-mm inside diameter (ID) fused-silica capillary column coated with a 0.25-µm bonded film of polyphenylmethylsilicone was used; J&W, DB-5 or equivalent.

4.1.12 Evaporative concentrator; Pierce Reacti-Vap evaporator and Reacti-Therm heating module or equivalent. The heat-block temperature needs to be maintained at 25°C.

4.1.13 GC/MS bench-top system; Hewlett-Packard, Model 5971 or equivalent.

Survey.

4.1.13.1 GC conditions: oven, 100°C (hold 5 minutes), and then program to 240°C at 6°C/min, then hold for 7 minutes; injection port, 240°C; carrier gas, helium; injection volume, 2 µL, splitless injection.

4.1.13.2 MS conditions: interface, 235°C; dwell time 20 milliseconds; mass ions monitored are listed in table 2 (in section 8 later in the report).

5. Reagents and consumable materials

5.1 Helium carrier gas, as contaminant free as possible (Grade 5).

5.2 Carbon dioxide gas for drying, high purity.

5.3 Nitrogen gas for evaporation, high purity.

5.4 SPE cartridges; Analytichem International, Bond-Elut No. 607313 or equivalent. The disposable cartridges are packed with 500 mg of silica coated with a chemically bonded C-18 hydrocarbon phase. The solid packing material is held in place with stainless-steel frits.

5.5 Disposable filter units; Rainin Instrument Co., Inc., Nylon-66 disposable syringe filter units or equivalent. Filters consist of a 25-mm diameter nylon membrane, nominal 0.45-µm pore diameter, enclosed in a nylon housing with Luer-Lok inlet and outlet fittings.

5.6 Glass-fiber filters (142-, 47-, or 25-mm diam.), nominal 0.7-µm pore diameter (GF/F grade); Whatman, Inc.

5.7 Stainless-steel filtration units (142-, 47-, or 25-mm diam.); Baxter Scientific Products.

5.8 Solvents: Hexane, isopropanol, methanol, and reagent water; B&J Brand, high-purity pesticide quality or equivalent.

5.9 Disposable glass capillaries, to fit the 50- and 100-µL, fixed- and variable-volume micropipettes; VWR Scientific. The glass capillaries are precleaned by baking at about 350ºC for 2 hours.

5.10 Stock standard solutions. Obtain the herbicides, metabolites, and internal standard either as pure materials from the U.S. Environmental Protection Agency's Pesticide and Industrial Chemicals Repository or as certified solutions from commercial vendors. If pure materials are obtained, prepare standard solutions by diluting 5 to 10 mg of the pure material with toluene in a 5- or 10-mL volumetric flask.

5.11 Primary fortification and dilution standard solutions. Use the individual stock standard solutions to prepare low-concentration (5 ng/µL)

and high-concentration (12.5 ng/μL) primary fortification and dilution standard solutions. Prepare these solutions by combining appropriate volumes of the stock standard solutions in a 2- or 5-mL volumetric flask and diluting with methanol. Add a 100-μL aliquot of the low-concentration or high-concentration solution to a 2-L water sample to obtain concentrations of 0.25 or 1.25 ng/μL for the method performance-evaluation studies. Use part of the high-concentration solution to prepare the calibration solutions.

5.12 Fortification solution of the polyaromatic hydrocarbon (PAH) internal standard. Prepare a solution of phenanthrene-d_{10} in toluene at a concentration of 50 ng/μL by diluting the stock standard solutions. Use part of this solution to prepare the calibration solutions. Dilute part of this solution to 5.0 ng/μL (add 200-μL to a 2-mL volumetric flask containing water) and use for adding to the sample eluants after nitrogen evaporation of the eluants to about 100 μL.

5.13 Surrogate standard solution. Prepare a solution of terbuthylazine in methanol at a concentration between 1.0 to 2.0 ng/μL. Add this solution to each sample prior to extraction by the SPE method (a 50-μL aliquot of this solution added to 100 mL of the sample should result in a concentration of between 0.5 to 1.0 μg/L of the surrogate).

5.14 Calibration solutions. Prepare a series of six calibration solutions in hexane-isopropanol (3:1) that contain all herbicides and metabolites at concentrations from 0.05 to 10.0 ng/μL and the PAH internal standard at a constant concentration of 0.25 ng/μL. Prepare these calibration solutions by appropriate dilutions of the high-concentration (12 ng/μL) primary fortification and dilution standard solution.

6. Sampling methods, sample-collection equipment, and cleaning procedures

6.1 Sampling methods. Use sampling methods capable of collecting water samples that accurately represent the water-quality characteristics of the surface water or ground water at a given time or location. Detailed descriptions of sampling methods used by the U.S. Geological Survey for obtaining depth- and width-integrated surface-water samples are given in Edwards and Glysson (1988) and Ward and Harr (in press). Similar descriptions of sampling methods for obtaining ground-water samples are given in Hardy and others (1989).

6.2 Sample-collection equipment. Use sample-collection equipment, including automatic samplers, that are free of plastic tubing, gaskets, and other parts that might leach interferences into water samples or sorb the herbicides and metabolites from the water. Use refrigerated, glass sample containers in automatic samplers that composite samples over time.

6.3 Cleaning procedures. Wash all sample-collection equipment with phosphate-free detergent, rinse with distilled or tap water to remove all traces of detergent, and finally rinse with high purity methanol (contained in a Teflon squeeze-bottle). Clean all sample-collection equipment before each sample is collected to prevent contamination of the samples.

7. Gas chromatograph/mass spectrometer performance

7.1 Gas chromatograph performance evaluation

The gas chromatograph performance normally is indicated by peak shape and by the variation of the target-compound (herbicide or metabolite) response factors relative to response factors obtained using a new capillary column and freshly prepared calibration solutions. If peak shape deteriorates or if response factors fail to meet the calibration criteria, either change the injection liner or perform maintenance on the capillary column to bring the gas chromatograph into compliance. Part of the inlet end of the capillary column can be removed to restore performance.

7.2 Mass spectrometer performance evaluation

7.2.1 Check the mass spectrometer prior to the analysis of any samples and every 24 hours thereafter during a series of analyses to ensure mass spectrometer performance according to the perfluorotributylamine (PFTBA) criteria outlined below. In addition, initially adjust the mass spectrometer to ensure that the established reporting level for each target compound can be achieved.

7.2.2 Tune the mass spectrometer daily using the procedure and standard software supplied by the manufacturer. Parameters in the tuning software initially optimize the resolution at masses 69, 131, 264, and 502 in the spectrum of PFTBA. Manually adjust the resolution so that the 131 and 219 ions are 100 ± 20 percent, and the 414 ion is 10 ± 5 percent relative to the abundance of the 131 and 219 ions.

8. Calibration

8.1 Initial calibration data are acquired by using a new capillary column and freshly prepared calibration solutions. These data are used in subsequent evaluation of the GC/MS performance.

8.2 Prior to the analysis of each sample set and every 24 hours thereafter during a series of analyses, analyze and evaluate a calibration solution (or solutions) containing all of the target compounds to ensure that the GC/MS performance is in compliance with the established criteria.

8.3 Acquire data for each calibration solution by injecting 2 µL of each solution into the GC/MS according to the GC/MS conditions described in paragraph 7.2. Calculate the relative retention time for each target compound and the surrogate compound (RRT_c) in the calibration solution or in a sample as follows:

$$RRT_c = \frac{RT_c}{RT_i} \quad , \tag{1}$$

where RT_c = uncorrected retention time of the quantitation ion of the target compound or surrogate compound; and

RT_i = uncorrected retention time of the quantitation ion of the internal standard (phenanthrene-d_{10}).

8.4 Calculate a response factor (RF_c) for each target compound and the surrogate compound in each calibration solution as follows:

$$RF_c = \frac{A_c \times C_i}{C_c \times A_i} \quad , \tag{2}$$

where A_c = GC peak area of the quantitation ion for the target compound or surrogate compound;

C_i = concentration of the internal standard, in nanograms per microliter;

C_c = concentration of the target compound or surrogate compound, in nanograms per microliter; and

A_i = GC peak area of the quantitation ion for the internal standard.

8.5 See table 2 for the respective quantitation ions and internal-standard reference used in these calculations. Use of the quantitation ions and internal standard specified is mandatory.

8.6 Initial calibration data acquired using a new capillary column and fresh calibration solutions are acceptable if the relative standard deviation is less than or equal to 35 percent for response factors calculated across the

Table 2.--*Retention time, relative retention time, quantitation ion, and confirmation ions for target compounds, surrogate compound, and internal standard*

[S, surrogate compound; IS, internal standard; m/z, mass per unit charge; --, not used]

Compound	Compound type or number	Retention time (minutes)	Relative retention time[1]	Quantitation ion (m/z)	Second confirmation ion (m/z)	Third confirmation ion (m/z)
Butylate	1	15.328	0.671	174	217	146
Vernolate	2	15.709	.687	128	86	43
Propachlor	3	19.437	.850	120	176	93
Cycloate	4	19.888	.870	154	--	--
Desisopropylatrazine	5	20.106	.880	158	160	91
Desethylatrazine	6	20.388	.892	172	187	58
Trifluralin	7	20.724	.907	306	264	335
Simazine	8	21.944	.960	201	186	173
Prometon	9	21.970	.961	210	225	168
Atrazine	10	22.149	.969	200	215	173
Propazine	11	22.312	.976	214	229	172
Terbuthylazine	S	22.487	.984	214	229	173
Phenanthrene-d_{10}	IS	22.86	1.000	188	--	--
Terbacil	14	23.395	1.023	161	160	116
Metribuzin	15	24.608	1.076	198	199	144
Simetryn	16	24.973	1.092	213	198	170
Ametryn	17	25.139	1.100	227	212	185
Alachlor	18	25.154	1.100	160	188	237
Prometryn	19	25.260	1.105	241	184	199
Bromacil	20	25.891	1.133	205	207	188
Metolachlor	21	26.453	1.157	162	238	146
Cyanazine	22	26.534	1.161	225	198	173
Diphenamid	23	27.222	1.191	167	72	239
Butachlor	24	29.045	1.271	176	160	188
Carboxin	25	30.2	1.321	143	235	87
Hexazinone	26	34.248	1.498	171	252	128

[1]Relative to phenanthrene-d_{10} internal standard.

working concentration range for each target compound or surrogate compound. Use the average response factors for the calibration-solution range in subsequent sample target-compound quantitation.

8.7 Subsequent daily response factors calculated for each compound need to agree within ± 20 percent of the average response factor for the target compound of interest. Analyze at least one calibration solution daily.

8.8 The latest response factors calculated can be added to prior response factors and a new average response factor calculated, provided the latest data meet the criteria given above and the relative standard deviation for all of the response-factor data is less than or equal to 35 percent.

8.9 Calibration-curve fitting routines also can be used, provided back calculation of the calibration-standard concentration agrees within ± 20 percent of the expected value.

9. Procedure

9.1 Set up the solid-phase-extraction vacuum manifold as shown in figure 1. Attach the SPE cartridges to the Luer-Lok fittings and twist counterclockwise to open the fittings. Preclean the SPE cartridges by rinsing with 3 mL of the elution solvent (hexane-isopropanol 3:1). Allow the solvent to drain by gravity, and then completely remove all solvent from the cartridge by either nitrogen positive pressure or vacuum. The clean cartridges can be stored in 40-mL glass vials until used.

9.2 Set up the solid-phase-extraction pumping apparatus as shown in figure 2. Rinse the Teflon-PFA tubing, pump, and in-line filter (if used) with methanol:water (1:1). Turn on the pump, and adjust the flow rate of the pump to 20 to 25 mL/min using a graduated cylinder to measure the volume through the SPE cartridge. Ensure there are no leaks in any of the fittings and that the sample bottle is vented to prevent negative pressures and bubbles from forming during sample pumping. If an in-line filter is used, flush all air from the lines before attaching the filter, otherwise air pockets will prevent flow through the filter, and the connections will leak.

9.3 Immediately before sample extraction, condition a SPE cartridge with 3 mL of methanol followed by 3 mL of reagent water by allowing the solvents to drain through the cartridge by gravity. About 10 minutes is required to allow the methanol and water to drip through the cartridge. Important: The SPE cartridge bed needs to be completely covered with methanol or water at all times once conditioning (or sampling) has begun.

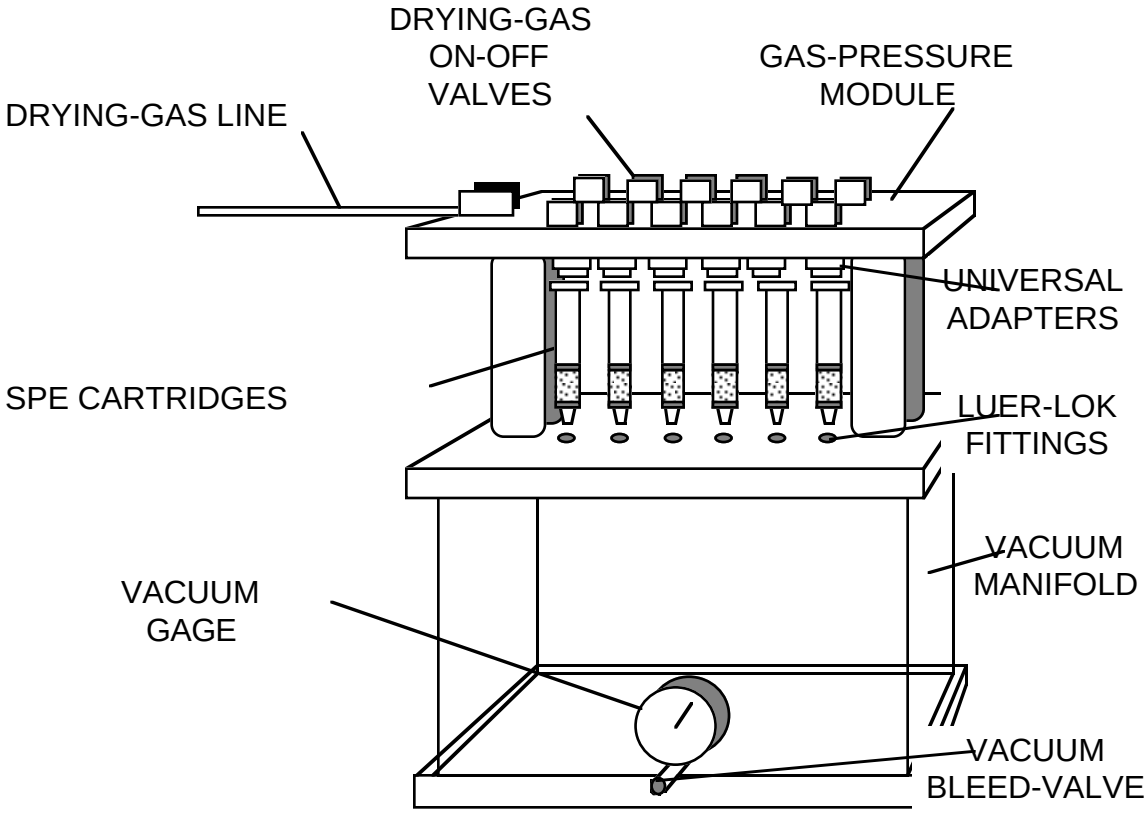

Figure 1.--Solid-phase-extraction (SPE) vacuum manifold.

9.4 Weigh the sample bottle to three significant figures, and record the gross sample weight. Add the methanol conditioner (1 percent of the sample volume) to the sample, and record the initial sample weight. Add a 50-µL aliquot of the terbuthylazine surrogate (5 ng/µL) using a micropipette with a disposable glass capillary. Swirl the sample in the bottle to thoroughly homogenize.

9.5 Place the inlet end of the Teflon-PFA tubing into the sample container, and turn on the pump to displace all air from the tubing. Attach the in-line filter (optional) and then the SPE cartridge, and begin collecting the sample that is pumped through the cartridge. Ensure that there are no leaks or sources of bubbles in the system. Small bubbles might form as the sample is pumped through the tubing, but they will not cause any problems if they accumulate in the pump head or filter unit. Large air bubbles are a problem because they can displace the methanol conditioner in the cartridge.

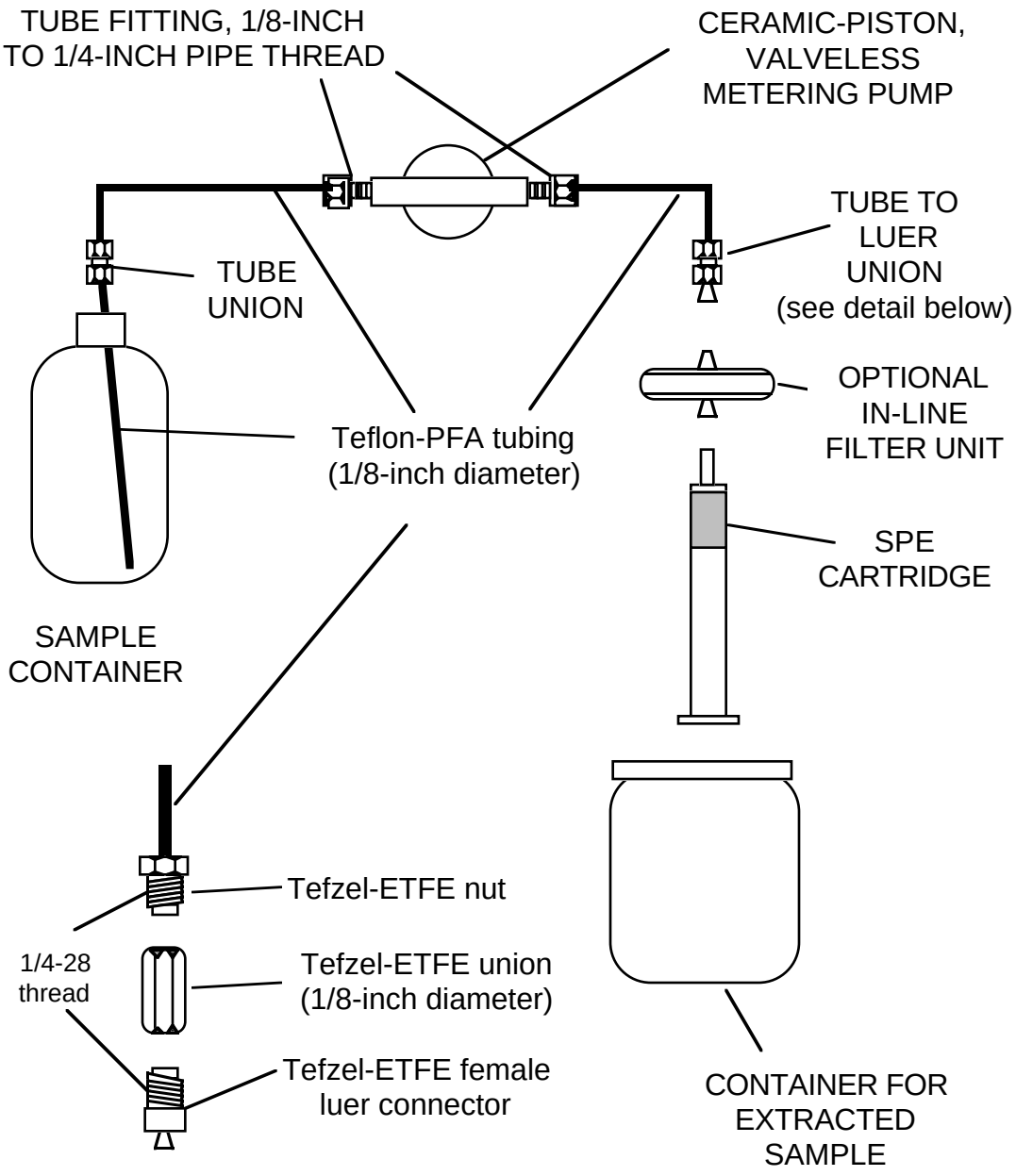

Figure 2.--Solid-phase-extraction (SPE) pumping apparatus.

9.6 Pump all of the sample through the SPE cartridge, and turn off the pump when completed. Disconnect the cartridge from the pump system, and remove residual interstitial water with a positive pressure of air. Weigh the extracted sample collected, and record the final weight of the sample processed through the cartridge. Discard the extended sample, weigh the empty sample bottle, and record the tare weight.

9.7 Rinse the pump and Teflon-PFA tubing with 50 mL methanol: water (1:1) to prepare for the next sample.

9.8 Attach a universal adapter to the large, open end of the SPE cartridge, then attach the adapter to the male Luer-Lok fitting on the gas-pressure module of the solid-phase-extraction vacuum manifold (fig. 1), and then dry the cartridge using a positive pressure (69 kPa for 15 minutes) of high purity carbon dioxide to remove all interstitial water. High purity nitrogen gas also can be used to dry the cartridge, but the necessary gas pressure and drying time will need to be determined.

9.8.1 Elute the analytes by attaching a syringe needle to the Luer-Lok end of the SPE cartridge, positioning the needle and cartridge above a 1.8-mL vial (fig. 3), and then adding 1.8 mL of the elution solvent to the cartridge and allowing the solvent to drain by gravity into the vial (about 5 minutes). Air pressure (using a 50-mL glass syringe) can be used to force any interstitial solvent remaining in the cartridge into the vial.

9.8.2 Concentrate the eluant in the 1.8-mL vial to about 100 µL under a gentle stream of nitrogen. At no time should the eluant be allowed to go dry, because this might result in loss of analytes. Add a 10-µL aliquot of the 5-ng/µL PAH internal-standard solution to the eluant, and extract 100 µL of the eluant into a 100-µL vial for GC/MS analysis.

10. Calculation and reporting of results

10.1 Sample analysis and data evaluation

Ensure that GC/MS conditions for the analysis of the target compounds in sample extracts are the same as those used in the analysis of the calibration solutions. Prior to the analysis of any sample extracts, ensure that the PFTBA mass-spectral performance criteria have been met, and that the target-compound calibration data conform to the criteria in paragraph 7.2. In addition, optimize the system so the reporting level for each target compound can be achieved. Inject 2 µL of the sample extract and acquire data using the GC/MS conditions described in paragraph 4.1.13.

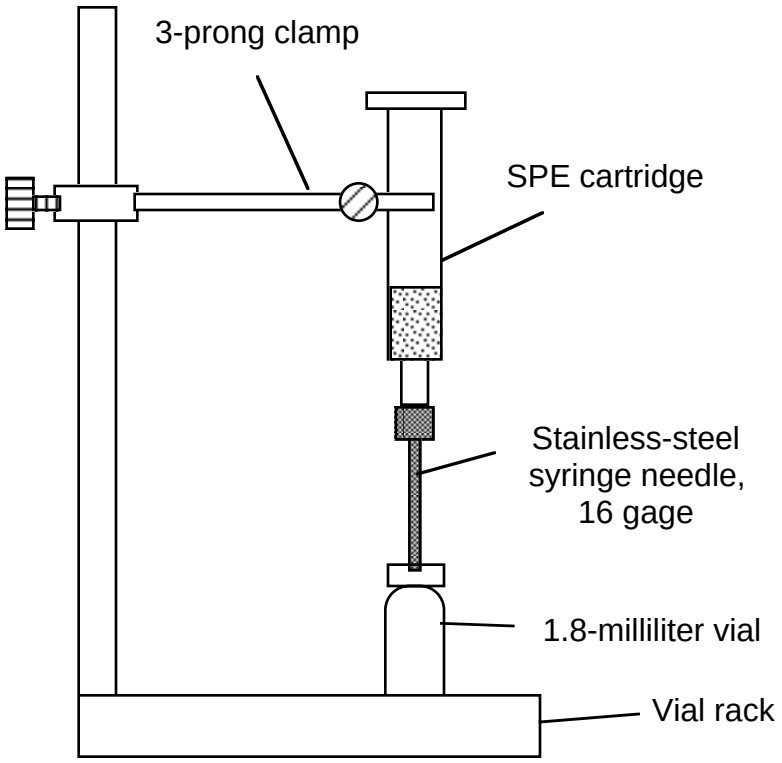

Figure 3.--Apparatus used for elution of analytes from solid-phase extraction (SPE) cartridges by gravity flow.

10.2 Qualitative identification

10.2.1 The expected retention time (RT) of the GC peak of the quantitation ion for the target compound of interest needs to be within ± 10 seconds of the expected retention time based on the RRT_c obtained from the internal-standard analysis. Calculate the expected retention time as follows:

$$RT = RRT_c \times RT_i \ , \qquad (3)$$

where RT = expected retention time of the target compound or surrogate compound;

RRT_c = relative retention time of the target compound or surrogate compound; and

RT_i = uncorrected retention time of the quantitation ion of the internal standard.

10.2.2 Mass-spectral verification for each target compound is done by comparing the relative integrated abundance values of the three significant ions monitored with the relative integrated abundance values obtained from calibration solutions analyzed by the GC/MS according to procedures given in paragraph 8. The relative ratios of the three ions need to be within ± 10 percent of the relative ratios of those obtained on injection of a 1-ng calibration solution.

10.3 Quantitation

10.3.1 If a target compound has passed the qualitative identification criteria above, calculate the concentration in the sample as follows:

$$C = \frac{C_i \times A_c \times 1000}{RF_c \times A_i \times W} \quad , \qquad (4)$$

where C = concentration of the target compound or surrogate compound in the sample, in micrograms per liter;

C_i = mass of the corresponding internal standard, in micrograms per sample;

A_c = area of the quantitation ion for the target compound or surrogate compound identified;

RF_c = factor for each target compound or surrogate compound calculated above;

A_i = area of the quantitation ion for the internal standard; and

W = weight of the sample extract, expressed in milliliters (1.0 g = 1.0 mL).

10.3.2 The percent recovery of the surrogate compound is calculated as follows:

$$R = \frac{C_i \times A_c}{RF_c \times A_i \times C_s \times V_s} \times 100 \quad , \qquad (5)$$

where R = percent of recovery of the surrogate compound;

C_i = concentration of the corresponding internal standard, in nanograms per sample;

A_c = area of the quantitation ion for the surrogate compound;

RF_c = response factor for the surrogate compound;

A_i = area of the quantitation ion for the internal standard;

C_s = concentration of the surrogate compound in the surrogate standard solution added to the sample, in nanograms per microliter; and

V_s = volume of the surrogate standard solution added to the sample, in milliliters.

10.4 Reporting concentrations

Report concentrations of organonitrogen herbicides as follows: If the concentration is less than the detection limit listed in table 2, report the concentration as less than the detection limit; if the concentration is greater than the detection limit, report the concentration to two significant figures.

METHOD PERFORMANCE

A reagent-water sample, a surface-water sample collected from the South Platte River in Colorado, and a ground-water sample collected in Jefferson County, Colo. (Arvada Well No. 14) were used to test the method performance. Each of the three samples was split into two subsamples. One set of three subsamples was fortified with 0.2 µg/L of each analyte and the other set of three subsamples was fortified with 2.0 µg/L of each analyte. Seven 100-mL aliquots of each of the six subsamples were analyzed in one laboratory (the National Water Quality Laboratory) using one GC/MS. Accuracy and precision data from the analyses are presented in tables 3-8.

With these data, a method detection limit (MDL) was calculated for each analyte using the formula:

$$MDL = S \times t\,(n-1, 1\text{-alpha} = 0.99), \quad (6)$$

where S = standard deviation of replicate analyses (micrograms per liter) at the lowest concentration; and

n = number of replicate analyses.

t (n-1, 1-alpha = 0.99): Student's t value for the 99 percent confidence level with n-1 degrees of freedom (Eichelberger and others, 1988).

Table 3.--*Accuracy and precision data from seven determinations of the method analytes at 0.2 microgram per liter in reagent water*

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Method detection limit (µg/L)
Butylate	0.081	0.014	17	41	0.052
Vernolate	.105	.024	23	53	.090
Propachlor	.164	.022	13	82	.080
Cycloate	.142	.026	18	71	.096
Desisopropylatrazine	.144	.010	7	72	.037
Desethylatrazine	.165	.026	16	82	.096
Trifluralin	.105	.004	4	52	.015
Simazine	.162	.029	18	81	.109
Prometon	.202	.019	9	101	.069
Atrazine	.134	.024	18	67	.088
Propazine	.133	.016	12	67	.059
Terbuthylazine	.137	.014	11	68	.054
Terbacil	.215	.025	11	107	.092
Metribuzin	.177	.014	8	89	.052
Simetryn	.168	.014	8	84	.050
Ametryn	.174	.016	9	87	.060
Alachlor	.203	.018	9	101	.067
Prometryn	.178	.019	11	89	.070
Bromacil	.301	.057	19	150	.213
Metolachlor	.229	.026	11	114	.097
Cyanazine	.219	.017	8	109	.063
Diphenamid	.230	.022	10	115	.083
Butachlor	.190	.023	12	95	.084
Carboxin	.240	.017	7	120	.064
Hexazinone	.248	.036	14	124	.132
Mean	**0.178**	**0.021**	**12**	**89**	**0.079**

Table 4.--*Accuracy and precision data from seven determinations of the method analytes at 2.0 micrograms per liter in reagent water*

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Butylate	0.811	0.053	7	41
Vernolate	1.107	.032	3	55
Propachlor	1.470	.061	4	73
Cycloate	1.338	.048	4	67
Desisopropylatrazine	.662	.073	11	33
Desethylatrazine	1.273	.072	6	64
Trifluralin	.460	.045	10	23
Simazine	1.250	.057	5	62
Prometon	1.236	.076	6	62
Atrazine	1.230	.044	4	61
Propazine	1.233	.049	4	62
Terbuthylazine	1.300	.037	3	65
Terbacil	1.618	.174	11	81
Metribuzin	1.505	.092	6	75
Simetryn	1.188	.109	9	59
Ametryn	1.320	.054	4	66
Alachlor	1.459	.064	4	73
Prometryn	1.328	.060	5	66
Bromacil	1.214	.199	16	61
Metolachlor	1.504	.096	6	75
Cyanazine	1.207	.175	14	60
Diphenamid	1.591	.093	6	80
Butachlor	1.392	.078	6	70
Carboxin	1.523	.116	8	76
Hexazinone	1.528	.100	7	76
Mean	**1.270**	**0.082**	**7**	**63**

Table 5.--*Accuracy and precision data from seven determinations of the method analytes at 0.2 microgram per liter in surface water (South Platte River)*

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Method detection limit (µg/L)
Butylate	0.116	0.014	12	58	0.051
Vernolate	.131	.026	20	66	.097
Propachlor	.198	.010	5	99	.036
Cycloate	.149	.011	8	74	.042
Desisopropylatrazine	.144	.005	4	72	.020
Desethylatrazine	.214	.052	24	107	.192
Trifluralin	.124	.009	7	62	.032
Simazine	.177	.009	5	88	.032
Prometon	.235	.011	5	118	.041
Atrazine	.151	.008	5	75	.028
Propazine	.147	.008	6	74	.031
Terbuthylazine	.156	.009	6	78	.034
Terbacil	.300	.014	5	150	.053
Metribuzin	.201	.010	5	101	.036
Simetryn	.189	.009	5	94	.033
Ametryn	.174	.009	5	87	.035
Alachlor	.215	.011	5	107	.042
Prometryn	.177	.017	10	88	.064
Bromacil	.375	.026	7	187	.096
Metolachlor	.244	.025	10	122	.093
Cyanazine	.282	.022	8	141	.082
Diphenamid	.260	.018	7	130	.066
Butachlor	.252	.021	8	126	.079
Carboxin	.260	.015	6	130	.056
Hexazinone	.279	.017	6	139	.062
Mean	**0.206**	**0.015**	**8**	**103**	**0.057**

Table 6.--*Accuracy and precision data from seven determinations of the method analytes at 2.0 micrograms per liter in surface water (South Platte River)*

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Butylate	0.851	0.090	11	43
Vernolate	1.139	.090	8	57
Propachlor	1.498	.070	5	75
Cycloate	1.258	.107	9	63
Desisopropylatrazine	.959	.107	11	48
Desethylatrazine	1.365	.104	8	68
Trifluralin	.551	.046	8	28
Simazine	1.253	.069	6	63
Prometon	1.552	.081	5	78
Atrazine	1.217	.072	6	61
Propazine	1.207	.077	6	60
Terbuthylazine	1.263	.068	5	63
Terbacil	2.016	.065	3	101
Metribuzin	1.602	.042	3	80
Simetryn	1.394	.090	6	70
Ametryn	1.361	.077	6	68
Alachlor	1.433	.059	4	72
Prometryn	1.333	.080	6	67
Bromacil	1.590	.069	4	80
Metolachlor	1.569	.066	4	78
Cyanazine	1.579	.059	4	79
Diphenamid	1.593	.084	5	80
Butachlor	1.504	.084	6	75
Carboxin	1.556	.111	7	78
Hexazinone	1.745	.089	5	87
Mean	**1.375**	**0.078**	**6**	**69**

Table 7.--*Accuracy and precision data from seven determinations of the method analytes at 0.2 microgram per liter in ground water (Arvada Well No. 14)*

[conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)	Method detection limit (µg/L)
Butylate	0.104	0.024	23	52	0.090
Vernolate	.141	.033	24	70	.123
Propachlor	.179	.026	14	90	.095
Cycloate	.151	.019	13	75	.072
Desisopropylatrazine	.145	.008	5	72	.028
Desethylatrazine	.153	.021	14	77	.078
Trifluralin	.111	.051	46	55	.188
Simazine	.169	.025	15	85	.093
Prometon	.188	.032	17	94	.118
Atrazine	.150	.026	17	75	.095
Propazine	.150	.024	16	75	.090
Terbuthylazine	.147	.027	18	74	.099
Terbacil	.252	.068	27	126	.252
Metribuzin	.194	.025	13	97	.095
Simetryn	.193	.030	16	97	.111
Ametryn	.190	.043	23	95	.159
Alachlor	.196	.024	12	98	.088
Prometryn	.188	.030	16	94	.112
Bromacil	.379	.056	15	189	.208
Metolachlor	.211	.028	13	106	.104
Cyanazine	.221	.018	8	111	.068
Diphenamid	.225	.041	18	113	.151
Butachlor	.197	.022	11	99	.082
Carboxin	.185	.027	15	93	.102
Hexazinone	.219	.033	15	109	.122
Mean	**0.186**	**0.030**	**17**	**93**	**0.113**

Table 8.--*Accuracy and precision data from seven determinations of the method analytes at 2.0 micrograms per liter in ground water (Arvada Well No. 14)*

[conc., concentration; µg/L, microgram per liter; --, not detected]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean accuracy (percent of true conc.)
Butylate	1.018	0.075	7	51
Vernolate	1.159	.090	8	58
Propachlor	1.518	.132	9	76
Cycloate	1.330	.103	8	67
Desisopropylatrazine	.636	.060	9	32
Desethylatrazine	1.337	.112	8	67
Trifluralin	.666	.112	17	33
Simazine	1.331	.077	6	67
Prometon	1.486	.124	8	74
Atrazine	1.253	.070	6	63
Propazine	1.305	.072	6	65
Terbuthylazine	--	--	--	--
Terbacil	1.651	.101	6	83
Metribuzin	1.451	.155	11	73
Simetryn	1.427	.157	11	71
Ametryn	1.348	.145	11	67
Alachlor	1.433	.128	9	72
Prometryn	1.350	.136	10	67
Bromacil	1.378	.129	9	69
Metolachlor	1.539	.146	10	77
Cyanazine	1.219	.090	7	61
Diphenamid	1.503	.160	11	75
Butachlor	1.381	.150	11	69
Carboxin	1.297	.141	11	65
Hexazinone	1.647	.155	9	82
Mean	**1.319**	**0.118**	**9**	**66**

MDLs are sample-matrix and compound dependent. MDLs calculated for reagent water at the 0.2 µg/L concentration range from 0.015 to 0.213 µg/L and have a mean of 0.079 µg/L (table 3). For surface water (South Platte River), MDLs calculated at the 0.2 µg/L concentration range from 0.020 to 0.192 µg/L, and have a mean of 0.057 µg/L (table 5). For ground water (Arvada Well No. 14), MDLs calculated at the 0.2 µg/L concentration ranged from 0.028 to 0.252 µg/L, and have a mean of 0.113 µg/L (table 7).

The mean accuracies (recoveries) of the analytes were sample-matrix and concentration dependent. The mean accuracy of the analytes determined at 0.2 µg/L was 89 percent in reagent water (table 3), 103 percent in surface water (South Platte River) (table 5), and 93 percent in ground water (Arvada Well No. 14) (table 7). The mean accuracies of the method analytes determined at 2.0 µg/L were significantly less than at 0.2 µg/L ($p < 0.001$, Mann-Whitney nonparametric test for two groups). The lesser recoveries at higher concentrations could be the result of problems with adding the 2.0 µg/L concentration solution mixture to the water samples. The relative concentration of water-immiscible solvent in the 2.0-µg/L concentration solution mixture was 69 percent, compared to 25 percent in the 0.2-µg/L samples. Solvent rinses of the sample bottles after the sample was pumped through the cartridge might help determine if sorption losses to the sample container was the cause of the lesser recoveries in the 2.0-µg/L concentration solution mixture.

The method is ideally suited for using automated laboratory systems for sample preparation. Preliminary testing of the method, with minor modifications, has been conducted using a Waters Millilab Workstation. The modifications included use of nitrogen, rather than carbon dioxide as a drying gas, and use of Waters Sep-Pak cartridges, rather than the Analytichem cartridges. The results indicated no significant differences in recovery of the 23 herbicides and 2 metabolites compared to the manual method described in this report.

CONCLUSIONS

From the data presented, SPE with GC/MS in SIM is an efficient and accurate method for determination of organonitrogen herbicides in environmental water samples. Recoveries averaged 80 to 115 percent for the 23 herbicides and 2 metabolites in a reagent-water sample and 2 natural-water samples fortified at levels of 0.2 and 2.0 micrograms per liter. The MDLs, based on a 100-mL sample size, range from 0.015 to 0.252 microgram per liter, and are dependent on sample matrix and specific herbicide.

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